

**FINAL REPORT—BERKELEY PIT INNOVATIVE
TECHNOLOGIES PROJECTS:
TECHNICAL ASSISTANCE INTERNATIONAL, INC.,
AND THE GROUP OF SCIENTISTS
DEMONSTRATION**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 7**

Prepared by

Montana Tech of The University of Montana
1300 W. Park Street
Butte, Montana 59701
Report # 7-MT-002-A

and

MSE Technology Applications, Inc.
200 Technology Way
P.O. Box 4078
Butte, Montana 59702

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and

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REVIEWS AND APPROVALS:

Prepared by: _____
Project Engineer

Reviewed by: _____
Project Manager

Approved by: _____

March 1997

Final Report—Berkeley Pit Innovative Technologies Projects: Technical Assistance International, Inc., and the Group of Scientists Demonstration

Demonstration performed by

Technical Assistance International, Inc.
1320 Loma Verde Drive
El Paso, Texas 79936

and

The Group of Scientists
Moscow State University
Vorobievsky Gory
Moscow, Russia 119899

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June 24 - July 12, 1996

Foreword

Today industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis. This supports the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc. (MSE), and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communication link between the researcher and the user community.

The objective of this demonstration was to remove metals, ions, and dissolved solids from the input Berkeley Pit water and to produce water that is fully compliant with Federal, State, and local water standards.

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Executive Summary

Under contract to the Mine Waste Technology Program (MWTP) of Montana Tech of The University of Montana (Montana Tech) in Butte, Montana, Technical Assistance International, Inc. (T/AI), conducted a bench-scale demonstration of an advanced process for producing statutorily compliant water and for removing and separating marketable metals from large volumes of Berkeley Pit water.

The innovative remediation technologies conducted during this demonstration have shown the following:

- the ability of T/AI's process to produce fully compliant effluent water;
- the ability of T/AI's process to remediate Berkeley Pit water without consuming external reagents;
- the ability of T/AI's process to regenerate the ion-exchange resins circulating in the process by reagents produced from constituents of the input Berkeley Pit water;
- the ability of T/AI's process to extract greater than 99.99% of all ionic components from the input Berkeley Pit water;
- the ability of T/AI's process to remove dissolved and suspended solids contained in the Berkeley Pit water in amounts greater than 99.99%; and
- the ability of T/AI's process to reduce sulfate ions to below detectable limits.

In addition, target pH for output water from the T/AI technological process ranged from a pH of 6 to 7.5. All pH measurements of process output waters made at the demonstration site immediately after obtaining resulting water were within this acceptable range.

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1. Introduction

1.1 Contract

Under contract to the Mine Waste Technology Program (MWTP) of Montana Tech of The University of Montana (Montana Tech) in Butte, Montana, Technical Assistance International, Inc. (T/AI) conducted a bench-scale demonstration to remove metals and to produce compliant waters from water retrieved from the Berkeley Pit. T/AI provided personnel, materials, and technologies required for the demonstration.

The term “compliant waters,” as used throughout this report, indicates the output water from the demonstration fully meets and is compliant with those standards for process output water as established by the Quality Assurance Project Plan (QAPP) - NRML Ci ID#Z-937-B.

Preparation for the demonstration took place in Moscow, Russia, from March 15 through June 15, 1996, and the final demonstration took place at Montana Tech from June 24 through July 12, 1996.

1.2 Requirement

As indicated by the QAPP, the only demonstration requirement was to produce water, from raw Berkeley Pit water, that met minimum Federal, State, and local standards and was suitable for discharge into the surface aquifer. This demonstration objective was met.

This report deals exclusively with the activities associated with producing fully compliant water from the Berkeley Pit input water. All subsequent materials presented in this report deal with achieving the demonstration objective.

Appendix C deals exclusively with the achievement of the “unofficial” demonstration objectives that were developed by T/AI. T/AI’s goal for this demonstration was to efficiently extract metals in a form of purity and concentration suitable for commercial sale.

1.3 Quality Assurance Project Plan

The approved QAPP is made part of this report by reference. Technical and program materials contained in the QAPP will be repeated only to the extent required to ensure clarity of this report.

The bench-scale demonstration’s performance-based requirements were to remove ions and dissolved metals and solids from the Berkeley Pit water and to produce water that is fully compliant with applicable Federal and State standards.

1.4 Evaluation Standards

Evaluation standards as stated in the QAPP were followed for the demonstration. Applicable quantitative and qualitative standards for compliant water as established by Federal, State, and local standards for liquids and solids produced and released into the environment were also observed.

Specific elements, ions, and dissolved and suspended solids and the concentrations in milligrams per liter (mg/L) in which these elements were found in the Berkeley Pit waters are presented in Table 1-1. Also presented are the statutory maximum limits, where known, of these elements in any effluent process stream.

Table1-1 illustrates those elements and ions that must be removed from the Berkeley Pit water to meet applicable water quality standards and QAPP requirements. The “must” determination is made because actual Berkeley Pit input levels are greater than allowable statutory maximum limits. The “Butte Demo” column indicates those elements and ions that need to be separated and removed from the input

waters. Those elements that could be removed, if proven economical to do so, are indicated by “\$Value?.” Both categories of elements were removed by the demonstration process. Elements designated as “Removal” were considered as waste for appropriate disposal; those elements designated as “Separation” were candidates for separation technologies as discussed in Appendix C.

Table 1-1. Elements removed during process.

Element	On RRP List	In Pit mg/L	Statute Max. mg/L	Actual > Statute = Removal	Butte Demo
Al	XX	260	2	Must	Separation
As	XX	0.8	0.36	Must	Removal
Ca		456		\$Value?	Separation
Cd	XX	2.14	0.01	Must	Removal
Cu	XX	172	1.3	Must	Separation
Fe	XX	1,068	1	Must	Separation
Mg		409		\$Value?	Separation
Mn	XX	185	0.05	Must	Separation
Na		76.5		\$Value?	Removal
Se	XX	0.4	0.26	Must	Removal
SO ₄	XX	7,600	500	Must	Removal
Zn	XX	550	5	Must	Separation
*RRP= Resource Recovery Project					

2. Full-Scale Process Description

2.1 General

The full-scale T/AI processing system consists of a combination of techniques, technologies, and processes that extract target substances and separate selected metals of commercial value from the Berkeley Pit water and, as a result, produce compliant water.

T/AI's technology uses:

- on exchangers to effect changes in pH resulting in selective precipitation of metals;
- on exchangers to decrease concentrations of soluble compounds in solution;
- molecular sorption of electrolytes by ion exchanger (not ion exchange) for separation of some metals;
- traditional ion-exchange processes for finishing water purification; and
- novel no-waste techniques to regenerate ion exchangers.

In the absence of a simple, more suitable, and readily understood term, this complex technological system is initially characterized as being predominantly "ion-exchange" technology. This characterization, unfortunately, leads the Western evaluator to compare T/AI's "ion-exchanger" technology with ineffective "ion-exchange" technologies that have been extensively evaluated in America. Such technologies have been found inadequate at extracting ions from, and correcting the pH of, large volumes of acidic waters, such as the Berkeley Pit matrix. This stereotypical characterization of T/AI's total effective processing package as being one of ion exchange is unfair to both the evaluator, as well as to the specific process.

To dispel this unfortunate but understandable connection with past ion-exchange technologies, T/AI's technological system will cease to be characterized as one of ion exchange and will

now be referred to as a precipitation-induced technology (PIT) system. The term "ion exchange" will only be used to describe those parts of T/AI's system that are identical to traditional "ion-exchange" technologies known in the West.

An itemized statement of the PIT processing system's general characteristic is as follows:

1. To label the "PIT processing system" exclusively as ion exchange and to equate it with traditional ion-exchange technologies does a disservice to T/AI's technology and the evaluation process.
2. Only part of the "PIT processing system" includes traditional ion exchange in the sense commonly understood and practiced in the West.
3. New techniques and procedures, both ion exchange and processing, are introduced via the "PIT processing system," including:
 - C Proprietary equipment and processing technologies allowing nonclogging precipitation to take place in direct association with ion-exchange processes.
 - C Proprietary pretreatment of resins that imparts novel chemical and process capabilities to commercially available resins.
 - C Proprietary chemical and process technologies for eluting, regenerating, and flushing ionite resulting in extended ionite life and yielding concentrated solutions containing extracted metals.
 - C A process capable of batch and/or continuous operational modes.

- C A process resulting in low consumption of resins (3 to 6% per year).
 - C A process developing all required reagents from input Berkeley Pit waters; no requirement for major external reagents.
 - C Recirculation, use, and reuse of all reagents, elutants, flushing solutions, and extractions associated with the processes.
4. No requirement for lime and/or limestone pretreatment, resulting in significantly less sludge production.
 5. No requirement for separating marketable metals from the lime and/or limestone precipitated sludge. Marketable metals are available directly as metal hydroxides for further processing.
 6. No direct or indirect adverse environmental impact.
 7. In part, use of well-known principles of fractional or selective precipitation.

2.2 Process Flowsheet

The complete PIT processing system is figuratively portrayed in Figure 2-1; however, a detailed description of this system is also provided in the proceeding sections. Certain critical elements of the system, which are considered proprietary or whose disclosure might later jeopardize the granting of international patents, are noted as being proprietary. While full disclosure of the PIT processes cannot be made at this time, the system's ability to produce fully compliant Berkeley Pit water speaks for the effectiveness of the proprietary process elements.

2.2.1 pH Change and Precipitation of Fe, Cu, Al, and Zn

atmospheric air-sparging techniques, Apparatus 1 transformed ferrous ions (Fe^{2+}) to the ferric (Fe^{3+}) state. Apparatus 1 and its proprietary anion-exchange resin also changed the pH of the input wastestream resulting in precipitation of greater than 99% of the iron (Fe), copper (Cu), aluminum (Al), and zinc (Zn) contained in the input Berkeley Pit water. The subject elements were precipitated in their hydroxide forms.

Apparatus 1 is not a traditional ion-exchange column. The apparatus is proprietary in both design and function using certain characteristics of the traditional ion-exchange process to change the process flow of the streams pH while using specially prepared ion-exchange resins.

The unique processes involved in Apparatus 1 ensure the ion-exchange resins or the apparatus in which these resins are contained will not become clogged with the resulting precipitate.

The ion-exchange process in Apparatus 1 removed a significant percentage of sulfate ions (SO_4) and replaced SO_4 with hydroxide (OH) ions. As a result, the pH of the water changed from 2.85 to approximately 5 to 5.5. Additionally, this SO_4/OH ion replacement formed metal hydroxides of Fe, Cu, Al, and Zn that are insoluble in water at the near neutral pH and that will form a precipitate.

2.2.2 Metal Hydroxide Separation

Insoluble metal hydroxides and the depleted anion-exchange resin (now in the RSO_4 form) were transported to Apparatus 2 and Apparatus 7. The precipitate and depleted ion-exchange resin were filtered from the on-going water stream by using drum/vacuum extraction, conventional filtering, and/or settling techniques as a practical method of satisfying throughput requirements. Because manganese (Mn), magnesium (Mg), calcium (Ca), and sodium (Na) do not form insoluble hydroxides at a neutral pH, they did not precipitate in

Berkeley Pit water was delivered to Apparatus 1 containing a specially prepared anion-exchange resin in the $R(OH)^-$ form. Using common

Apparatus 2 but were transported to following stages where these elements were extracted.

Figure 2-1. Process flow diagram.

The sludge containing Fe, Cu, Al, and Zn hydroxides and depleted ionite were treated with sulfuric acid (H_2SO_4) in Apparatus 7, which converted the metal hydroxides into metal sulfates in concentrated solution. The resin component of the input sludge was, therefore, separated from its commingled precipitate with these liberated resins being sent to Apparatus 4 for a proprietary process resulting in ROH-form resin with special chemical properties. Regenerated resins were then returned to Apparatus 1 and reused as the primary agent causing a change in pH and precipitation of input Berkeley Pit water.

The solution of Fe, Cu, Al, and Zn sulfates was passed to a second section of Apparatus 7 for separation and purification by selective or fractional precipitation, chromatography, or other methods to be later selected as appropriate in producing the final commercial product. Details of the separation and purification processes of metal sulfates are presented in Appendix C.

2.2.3 Processing of Solution Containing Compounds of Mn, Mg, Ca, and Na

The solution with a pH of 5 to 5.5 and containing sulfates of Mn, Mg, Ca, and Na that remained after the precipitation processes in Stages 1 and 2 was processed in the final section of Stage 2.

Processing herein was designed to remove all Mn and Mg present in the process stream. Processing techniques used were either selective or fractional precipitation in either a batch or a continuous mode of operation. Centrifugal or settling and/or filtration techniques were used to extract the precipitates at the appropriate points of the process. Details of the Mn and Mg separation and purification processes are presented in Appendix C.

Once the Mn and Mg concentrations were removed to quantities undetectable by inductively coupled plasma (ICP) analytical techniques, the primary constituents of the process stream were Ca and Na in sulfate form. This solution was

treated in a traditional ion-exchange column where the sulfates were transferred to hydroxides and the resultant process stream contained hydroxides of Ca and Na. This process stream was the input to Stage 3.

2.2.4 Removal of Ca and Na from the Process Stream

Calcium and Na were removed from the process stream in sequential fashion with Ca being removed first. There was no statutory reason for removing Ca and Na ions from the output water stream since standards had not been established for these two elements. However, to ensure “low” levels of these ions and to remove any remaining micro-amounts of heavy metals, two final “polishing” operations were employed. Both operations were contained in Stage 3.

The first operation in Stage 3 extracted Ca in a column with cation-exchange resin in the Na form, which was obtained from the successive operation in Stage 3. The output solution from this first operation contained primarily sodium hydroxide (NaOH), and this solution was passed on to the second part of Stage 3 where NaOH was removed using a traditional ion-exchange column on cation-exchange resins of the H^+ form.

The ion-exchange reaction in Apparatus 3 produced demineralized and deionized water. At this point, water leaving this cation-exchange process is believed to be compliant with applicable Federal, State, and local standards for waters to be discharged into the environment and is suitable for industrial or agricultural use and/or human consumption.

2.2.5 Regeneration of Ion-Exchange Resins

Depleted ion-exchange resins from Apparatus 1 and Apparatus 3 were passed to proprietary counter-current resin regeneration processes in Apparatus 4 and Apparatus 5. The anion-exchange resin was treated with an NaOH

solution in Apparatus 4, and the cation-exchange resin was treated with H_2SO_4 in Apparatus 5 in proprietary processes developed by T/AI. Additional proprietary operations related to flushing, rinsing, and eluting were performed on these resins during the regeneration processes, resulting in ionites of the properties required by Stages 1 and 3.

The anion-exchange resins were regenerated using NaOH from the electrolyzer and produced sodium sulfate (Na_2SO_4), which was directed to the electrolyzer where it was converted into NaOH and H_2SO_4 . Some micro-amounts of metals may have been eluted in the regeneration of cation-exchange resins and passed to the electrolyzer.

The cation exchanger was regenerated using H_2SO_4 from the electrolyzer and produced the gypsum precipitate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Na_2SO_4 solution. The Na_2SO_4 solution was directed to the electrolyzer.

A particularly important feature of the regeneration process was that only the precise amount of required reagents was supplied and consumed, and no amount of processing reagents was wasted.

Regeneration of the ion-exchange resins in counter-current columns reduced the amount of ion-exchange resin being consumed in the process and further decreased the equipment volumes.

2.2.6 Electrolyzer

Sulfate solutions in the form of Na_2SO_4 from both the cation and anion exchangers regeneration processes were provided as an input to the electrolyzer (Apparatus 6). Electrolysis of alkali metal salts produced reagents NaOH and a mixture of Na_2SO_4 and H_2SO_4 . These reagents were used in the ion-exchange regeneration processes in Apparatus 4 and Apparatus 5 and

Calculations based on the composition of Berkeley Pit water indicated the electrolyzer will produce 105 to 110% of the NaOH required for anion-exchange resin regeneration and approximately 1,000% of the H_2SO_4 required for cation-exchange regeneration. The result was a surplus of these two commodities. Part of the surplus H_2SO_4 was used to dissolve the metal hydroxides in Apparatus 7; however, but there was still an excess of H_2SO_4 .

Recirculation of the treated Na_2SO_4 solutions took place between Apparatus 4 and Apparatus 6 (Na_2SO_4 and NaOH) and Apparatus 5 and Apparatus 6 (Na_2SO_4 and H_2SO_4).

The electrolyzer process proposed herein was one covered by U.S. Patent Number 4,561,945, currently owned by Denora, an Italian Corporation.

The proposed processes for removing ions and suspended solids from Berkeley Pit water were largely based on the precipitation of metal hydroxides in Stages 1 and 2. Such precipitation can only be achieved by increasing the pH of the water. The increases in process stream pH are traditionally achieved by adding a base (Ca) in the form of a lime slurry ($\text{Ca}(\text{OH})_2$) or limestone as one of the first process steps, thus increasing the pH from 2.65 towards neutral values of approximately 5.5 and then ultimately to a pH of 10.

Note that the precipitate traditionally created by adding lime or limestone to the Berkeley Pit water contains hydroxides of little value. To later separate and extract these metals from the huge amounts of precipitate is complicated and expensive. In the process, only the metals in hydroxide form were precipitated in this initial stage, and the processes of filtration and separation were simple, straightforward, and relatively inexpensive.

were used to dissolve metal hydroxides as may be required in the first stage of Apparatus 7.

In such traditional processes, lime must be purchased and transported to the treatment site in large quantities, ground, mixed with water to form a slurry, and then added to the input process stream in the proper amounts to achieve the desired pH adjustment. Subsequent to precipitation, large amounts of gypsum (CaSO_4) in the cake form must be disposed as either waste or a commercial product (generally the gypsum is considered waste due to its very limited commercial value in today's marketplace). The proposed electrolyzer eliminates the need for lime in creating the base used as the precipitation and pH adjustment agent. The electrolyzer produces sufficient quantities of a basic reagent (NaOH) to satisfy the demands of the proposed processes.

A further requirement of the proposed process is to transform the metal hydroxide precipitate into a sulfate at Stage 7. This transformation is affected by dissolving the precipitated hydroxides with H_2SO_4 . The required H_2SO_4 reagent is traditionally purchased and represents an expense to the process. However, the proposed electrolyzer eliminates the need to purchase the required H_2SO_4 reagent. The electrolyzer produces sufficient quantities of the acid reagent H_2SO_4 to satisfy the demands of the proposed processes.

The purposes of the electrolyzer are to eliminate the need and related expense for the basic reagent affecting the change of the solution's pH and the acid reagent affecting dissolution of the precipitated hydroxides. The electrolyzer uses ions, Na^+ and SO_4^{2-} , present in the input Berkeley Pit process stream to produce the base

reagent (NaOH) required for pH adjustment and regeneration of anion exchanger in Stage 4. It also produces the acidic reagent (H_2SO_4) required for dissolving the metal hydroxides in precipitate in Stage 7 and for regenerating the cation exchanger in Stage 5. Therefore, large quantities of SO_4 and Na ions present in the input process stream are simultaneously removed and converted into reagents that otherwise have to be purchased as inputs to the process.

Production of the H_2SO_4 and NaOH is affected by the electrolyzer process by patented technological processes and by the electricity's energy source.

Examination of the patent literature, discussions with the patent holder, and T/AI's independent calculations led to the conclusion that the expense for creating the two reagents is approximately 13 kilowatt (kW) per cubic meter of water processed. This expense for electrical power should be significantly less than the expenses for the purchase, transportation, storage, and processing of lime; expenses related to the disposal of the gypsum sludge; and the purchase of sulfuric acid reagent. However, the detailed economic equation has not been solved because some of the basic cost elements remain unknown.

As stated above, the calculations indicate that a surplus of reagents NaOH and H_2SO_4 will be produced. These calculations relate directly to the amount of Na and SO_4 ions present in the input process stream. Aside from the obvious approach of selling the excess of these two reagents, the process can be adjusted to produce only the required amount of NaOH and H_2SO_4 , thus eliminating the excesses.

3. Bench-Scale Demonstration

The demonstration in Butte, Montana, was conducted during a 3-week period from June 24 through July 12, 1996. Preparation activities took place during the first week of this period, and demonstration activities occupied the final 2 weeks.

Demonstration schedules were divided into two major phases: predemonstration or preparatory activities, which took place in Russia, and the actual demonstration, which took place in a laboratory at Montana Tech of The University of Montana (Montana Tech) in Butte, Montana. Activities within each phase proceeded logically and were related to the stages of the processes to be demonstrated. Complete demonstration schedules are presented in Figure 3-1.

T/AI personnel at the Butte demonstration site were:

Project Manager: Hayward S. Melville, Technical Assistance International, El Paso, Texas, (915) 858 7056

Principal Investigator: Nikolai B. Ferapontov, Ph.D., Moscow State University, Moscow, Russia, 011 7 095 939 4019

Sorbent Scientist: Vladimir I. Gorshkov, Sc.D., Moscow State University, Moscow, Russia, 011 7 095 939 4019

Materials Extraction Scientist: Vladimir A. Ivanov, Ph.D., Moscow State University, Moscow, Russia, 011 7 095 939 4019

Process Engineer: Ivan V. Bazarov, M.S., Technical Assistance International, Moscow, Russia, 011 7 095 134 5344

Support personnel from Montana Tech present at the demonstration were:

Project Manager, MWTP: Karl Burgher, Ph.D., P.E., Montana Tech of The University of Montana, (406) 496-4410

Assoc. Project Manager, MWTP, and Project Manager, Berkeley Pit Innovative

Technologies Project: Steve Anderson, M.S., Montana Tech of The University of Montana, (406) 496-4409

QA Manager and Project Engineer: Catherine Wassmann, Montana Tech of The University of Montana, (406) 496-4624

Analytical Support: Jennifer Saran, Montana Tech of The University of Montana, (406) 496-4627

3.1 Demonstration Objective

The project objective was to demonstrate the proposed technological process produces fully compliant water suitable for release into the surface aquifer. Specific limits for each constituent element of the Berkeley Pit matrix are stated in Table 1-1.

3.2 Demonstration Process

The demonstration process involved performing bench-scale chemical and processing operations that duplicated, to the extent possible, the processes and procedures as stated earlier in describing the full-scale PIT processing system for producing compliant water from Berkeley Pit water. QAPP requirements also defined the demonstration process.

In all cases, demonstration activities duplicated precisely the chemical technologies characterizing a full-scale implementation of T/AI's PIT processing system. Demonstration activities included the process flow of water and intermediate products through the proposed system.

The only stage of the proposed process not directly duplicated was Stage 6--the electrolyzer. This stage was to produce H_2SO_4 and $NaOH$, reagents used throughout the full-scale process from constituents of the input Berkeley Pit water.

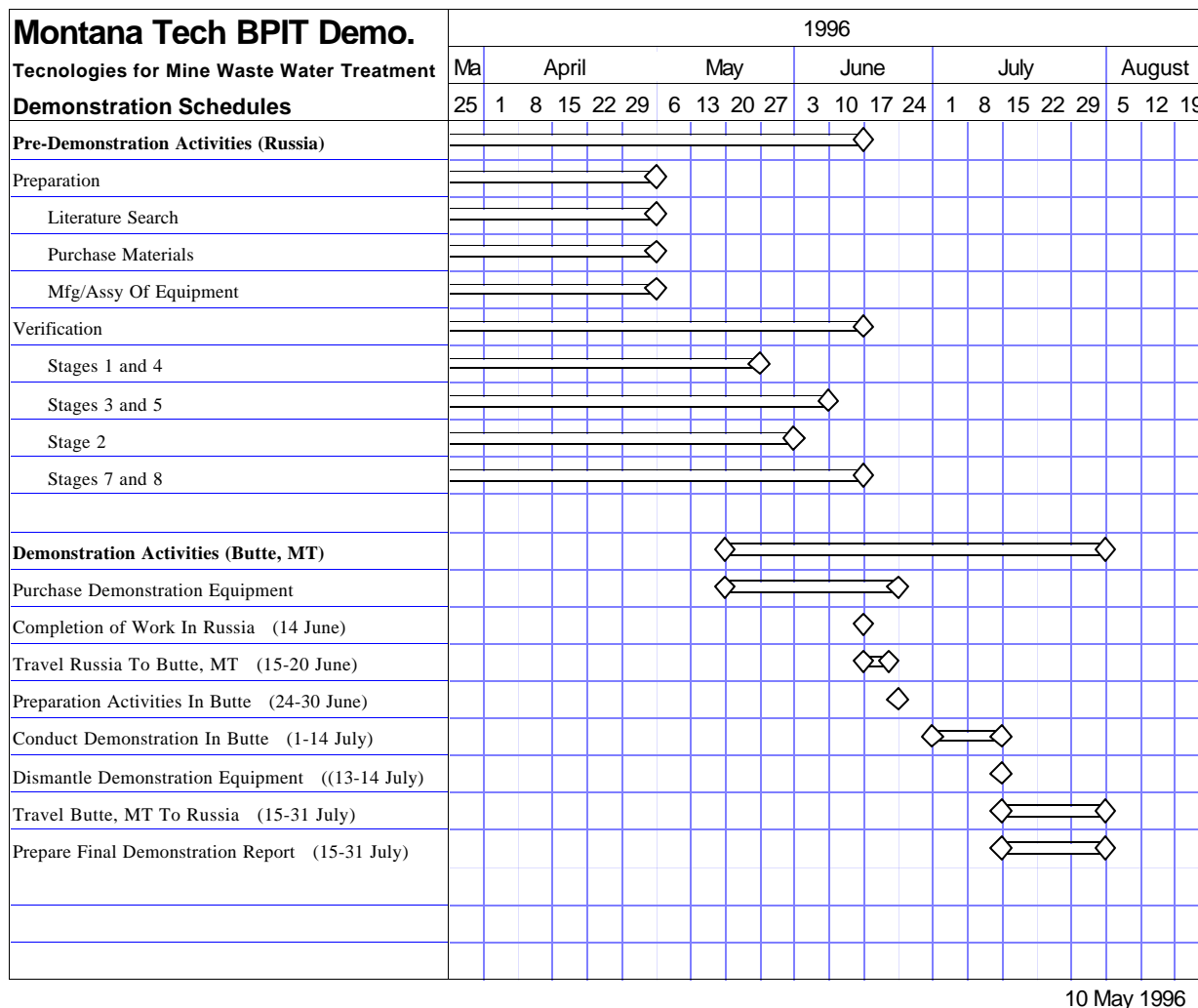


Figure 3-1. Demonstration project schedules.

Direct duplication of the electrolyzer was not

practical considering the financial constraints of the demonstration program and was not necessary since the H_2SO_4 and NaOH products can be directly substituted by reagents purchased for the process. Sulfuric acid and NaOH were purchased and substituted within the demonstration process for those products that would have been otherwise produced by the electrolyzer during Stage 6.

Preparatory activities consumed most of the first week's activities at the demonstration site. Such activities consisted of assembling required laboratory equipment; preparing required process reagents and required analytical reagent; preparing and conditioning proprietary ion-exchange resins; and preparing proprietary solutions for flushing, rinsing, eluting, and regenerating ion-exchange resins used throughout the process.

All demonstration processes were conducted in the “batch” or periodical mode of operation; no continuous operations were duplicated in the demonstration process.

Demonstration activities during the formal 2-week demonstration period were associated with processing Berkeley Pit water and producing compliant water for formal testing and evaluation. Available on-site ICP analytical capabilities were used extensively during the demonstration period.

3.3 Sample Collection

One sample of input and three samples of output water were taken on each of the following dates:

- C Tuesday July 2, 1996, at approximately 1:00 p.m.
- C Monday July 8, 1996, at approximately 1:00 p.m.
- C Wednesday July 10, 1996, at approximately 1:00 p.m.

Samples were taken by Montana Tech’s Berkeley Pit Innovative Technologies Project personnel according to methods and techniques stated in the QAPP.

Water samples were taken at sample points 1 and 5 within the processing system. These sample points were established and agreed to as part of the QAPP. Sample points 1 and 5 are described below:

C Sample Point: [1]

Purpose of Sample/Test: Determine quantitative and qualitative composition of untreated Berkeley Pit water as input to the demonstrated process.

Critical/Noncritical: Critical.

Performance Phase(s): Preparatory and Demonstration.

C Sample Point: [5]

Purpose of Sample/Test: Determine quantitative and qualitative composition of processed Berkeley Pit water from the demonstrated process.

Critical/Noncritical: Critical.

Performance Phase(s): Preparatory and Demonstration.

Analysis of all collected samples was performed by ACZ Laboratories, Inc. of Steamboat Springs, Colorado—an EPA-certified confirming laboratory.

3.4 Data Results

Values presented in Tables 3-1, 3-2, and 3-3 are in milligrams per liter (mg/L). Indications of BDL represent “Below Detectable Limits” as defined by the ICP analytical technique and specific instrument used by ACZ Laboratories. The Method Detection Limit (MDL) of each of the elements or ions measured is stated in the MDL column. These MDL figures are obtained from data sheets provided by ACZ Laboratories. However, the MDLs stated in the tables are for concentrations measured at sample point 5 and are different from the MDLs stated by ACZ Laboratories for concentrations measured at sample point 1. The differences are due to the dilutions necessary to analyze the untreated Berkeley Pit water at sample point 1.

Data listed in the tables is taken directly from the analytical results data sheets provided by ACZ Laboratories. Original analytical results data sheets are included in Appendix A.

Table 3-1. Sample T/AI 1 taken on July 2, 1996.

07/02/96 Element	Nominal In-Pit Level	Sample Point One	Point 5 Sample 1-1	Point 5 Sample 1-2	Point 5 Sample 1-3	MDL	Statute Max. Level
Al	260	307	0.09	BDL	BDL	0.030	2.00
As	0.8	BDL	BDL	BDL	BDL	0.020	0.36
Cd	2.14	2.18	BDL	BDL	BDL	0.003	0.01
Cu	172	197	BDL	BDL	BDL	0.010	1.30
Fe	1,068	936	0.05	BDL	BDL	0.010	1.00
Mn	185	222	BDL	BDL	BDL	0.005	0.05
Se	0.4	BDL	BDL	BDL	BDL	0.040	0.26
SO ₄	7,600	9,200	BDL	BDL	BDL	0.500	500.00
Zn	550	618	0.04	0.03	BDL	0.010	5.00
pH	2.65	2.80	5.20	5.20	5.20	0.100	6.0-9.0
BDL: Below Detection Limit							

Table 3-2. T/AI 2 taken on July 8, 1996.

07/08/96 Element	Nominal In-Pit Level	Sample Point One	Point 5 Sample 2-1	Point 5 Sample 2-2	Point 5 Sample 2-3	MDL	Statute Max. Level
Al	260	284	0.260	BDL	BDL	0.030	2.00
As	0.8	BDL	BDL	.040	BDL	0.020	0.36
Cd	2.14	2.04	BDL	BDL	BDL	0.003	0.01
Cu	172	182	BDL	BDL	BDL	0.010	1.30
Fe	1,068	918	.010	BDL	BDL	0.010	1.00
Mn	185	206	BDL	BDL	BDL	0.005	0.05
Se	0.4	0.08 J	BDL J	BDL J	BDL J	0.040	0.26
SO ₄	7,600	9,700	BDL	BDL	BDL	0.500	500.00
Zn	550	585	0.04	0.03	0.080	0.010	5.00
pH	2.65	2.80	6.40	6.0	6.0	0.100	6.0-9.0
BDL: Below Detection Limit							
J: The results are estimated							

Table 3-3. T/AI 3 taken on July 10, 1996.

07/10/96 Element	Nominal In-Pit Level	Sample Point One	Point 5 Sample 3-1	Point 5 Sample 3-2	Point 5 Sample 3-3	MDL	Statute Max. Level
Al	260	289.0	0.08	BDL	BDL	0.030	2.00
As	0.8	BDL	BDL	BDL	BDL	0.020	0.36
Cd	2.14	2.11	BDL	BDL	BDL	0.003	0.01
Cu	172	190.0	BDL	BDL	BDL	0.010	1.30
Fe	1,068	924.0	0.03	BDL	0.01	0.010	1.00
Mn	185	218.0	BDL	BDL	BDL	0.005	0.05
Se	0.4	BDL	BDL	BDL	BDL	0.040	0.26
SO ₄	7,600	9,800	BDL	BDL	BDL	0.500	500.00

Zn	550	609.0	0.02	BDL	0.03	0.010	5.00
pH	2.65	2.80	5.50	5.20	5.10	0.100	6.0-9.0
BDL: Below Detection Limit							

4. Conclusions

4.1 General

This bench-scale demonstration involving the remediation of Berkeley Pit water and conducted by the team of T/AI and The Group of Scientists of Moscow State University has shown the ability of the PIT processing system to:

- produce fully compliant effluent water;
- remediate the Berkeley Pit water without consuming external reagents;
- regenerate the ion-exchange resins circulating in the process by using reagents produced from constituents of the input Berkeley Pit water; and
- extract more than 99.99% of all ionic components from the input Berkeley Pit water.

4.2 pH

Target pH levels for output waters from the PIT processing system are in the range of 6 to 9. All pH measurements of process output waters at sample point 5 taken at the demonstration site immediately after obtaining resulting water were within this acceptable range.

The first and third lots of sample water sent to ACZ Laboratories were analyzed to have a pH of 5.1 to 5.5, which is unacceptable. ACZ Laboratories stated that the difference in pH levels between the demonstration site and the analytical laboratory is a common occurrence in waters of high purity since the slightest absorption of carbon dioxide (CO₂) will reduce the pH. T/AI's scientists agree with this statement.

4.3 SO₄

Sulfate ions (SO₄) were reduced to undetectable levels as measured by ACZ Laboratories' Ion Chromatography Analytical Instrument.

4.4 Consideration of Alternative Approach

This process is specifically designed to extract, separate, and concentrate metals of commercial value, while simultaneously producing pure and compliant effluent water. Each discrete process related to the extraction, separation, and concentration of metals is a cost contributor and their collective necessity should be carefully evaluated with respect the value of metals produced. If a cost-benefit analysis demonstrates that the economic benefit represented by the value of selected metals produced does not justify the related increase in project cost, an alternative and significantly lower cost process exists. Such a cost-benefit analysis has not been performed; therefore, clarification of the general statements made throughout this report cannot be presented at this time.

Production of fully compliant water from Berkeley Pit water can be achieved by using a low-cost alternative to T/AI's proposed process by simply removing those offending metal and sulfate ions by using anion exchangers in the OH form. Subsequent processing of the resultant filtrate requires significantly less amounts of ion exchangers than required by traditional ion-exchange demineralization processes.

4.5 Summary Diagram of Proposed Processes with Material Balances

A summary diagram of the technological process with accurate estimations of input and output amounts per cubic meter of input water is presented in Figure 4-1.

Figure 4-1. Summary diagram of the technological process.

Appendix A
Quality Control Summaries and Analytical Data Sheets

Appendix B

Resumes of Technical Assistance International, Inc., Scientific Personnel Performing The Demonstration

Principal Investigator: Nikolai B. Ferapontov, Ph.D.
Sorbent Scientist: Vladimir I. Gorshkov, Sc.D.
Materials Extraction Scientist: Vladimir A. Ivanov, Ph.D.
Process Engineer: Ivan V. Bazarov, M.S.

Position: Principal Investigator
Name: Nikolai B. Ferapontov
Education: Ph.D. in Physical Chemistry, Moscow State University
Experience: Research and development of new and effective physico-chemical bases, primarily ion-exchange sorption, for the separation of complex mixtures and the refinement and purification of extracted substances and metals.

Current research activity is concerned with non-ion-exchangeable interactions of electrolytes and ion exchangers, the dynamic properties of mass-exchange columns, and the mathematical modeling of complex ion-exchange processes.

Advisor of candidate of science (Ph.D.) students. Has written and published more than 60 scientific articles in both Russian and English and is the holder of 14 Russian patents.

Position: Senior Sorbent Scientist
Name: Vladimir I. Gorshkov
Education: Sc.D. in Physical Chemistry, Moscow State University
Experience: Currently Professor, Head of the Laboratory of Stable Isotopes, Faculty of the Department of Chemistry, Moscow State University. Member of Chromatography Scientific Council and High Purity Substances Council of The Russian Academy of Science.

Current research activity is in new and effective physico-chemical methods for the separation of complex mixtures, substances, or isotopes and the refinement and purification of extracted substances, metals, and isotopes. Primary methods of separation are ion-exchange, sorption, and chemical isotopic exchange. Studies include equilibrium and kinetics of ion and isotopic exchange, dynamic properties of mass exchange columns, and mathematical modeling of complex ion and isotopic exchange processes.

Teaching activities include advanced courses in physical chemistry, special courses in ion exchange, and theory of isotopic separation. Advisor of 38 Ph.D. candidates and 2 doctors of science.

Dr. Gorshkov has 40 years experience in the design and development and practical implementation of ion-exchange technologies. He has written and published more than 250 scientific articles, 1 book, 2 text books, and is the holder of more than 40 patents.

Position: Senior Materials Extraction Scientist
Name: Vladimir A. Ivanov
Education: Ph.D. in Physical Chemistry, Lomonosov Moscow State University
Experience: Research and development in physico-chemical bases for the separation and purification of substances, including stable isotopes and ionic solutes using ion-and chemical-exchange methods. Recent research activity has been concerned with the separation of cesium and rubidium from their binary mixtures and from mixtures with other alkali metals; recovery of strontium from concentrated solutions of complicated composition such as natural brines; production of nitrogen-15 from natural isotopic mixtures; reagentless dual-temperature purification of alkali metal compounds from alkali-earth and transition metals; and separation of sugar from molasses.

Dr. Ivanov teaches special courses on the “Theory of Isotopic Separation” and is advisor to several Ph.D. candidates.

Position: Process Engineer
Name: Bazarov, Ivan V.
Education: MS, Moscow Aviation Institute in Aircraft Engine Design and Process Control Instrumentation.
Experience: Research, design, development, and manufacture of chemical manufacturing equipment, aircraft turbine and liquid fuel engines, and related test and evaluation instrumentation. Progressive experience in the management of scientific and technological programs within Russian Governmental organizations and the United Nations. Spent 4 years with the United Nations Office for Science and Technology. Most recent experience as manager of industrial processes technology transfer.

Thirty years experience in design and development of process control systems and components, and management of scientific and technical personnel for Russian Government, United Nations, and industrial organizations.

Appendix C

Metals Extraction, Separation, and Concentration

C.1 Process Flowsheet

Figure C-1 is a block diagram level portrayal of the complete PIT processing system. A description of this system is herewith provided. Certain critical elements of the system, elements considered as proprietary or whose disclosure herein might later jeopardize the granting of international patents, are noted as being proprietary. While full and open disclosure of our processes can not be made at this time, the ability of the system to produce fully compliant water and extract, separate, and concentrate metals speaks for the effectiveness of those process elements designated as proprietary.

C.2 Target Ionic Components of the Berkeley Pit Input Matrix

Table C-1 lists those ions selected for removal and separation by the demonstration process.

C.3 pH Change and Precipitation of Fe, Cu, Al, and Zn

Berkeley Pit water is delivered to Apparatus 1 containing a specially prepared anion-exchange resin in the $R(OH)^-$ form. Using common atmospheric air-sparging techniques, apparatus 1 transforms ferrous ions (Fe^{2+}) to the ferric (Fe^{3+}) state. Apparatus 1 and its proprietary anion-exchange resin also changes the pH of the input wastestream resulting in precipitation of >99% of the Fe, Cu, Al, and Zn contained in the input acid mine drainage (AMD). The subject elements are precipitated in their hydroxide forms.

Apparatus 1 is not a traditional ion-exchange column, it is an apparatus proprietary in both design and function using certain characteristics of the ion-exchange process to change pH of the process flow stream while using specially prepared ion-exchange resins. Because of the unique and proprietary processes involved in

Apparatus 1, there is no possibility of the precipitate clogging the ion-exchange resins or the apparatus in which these resins are contained.

The ion-exchange process in Apparatus 1 results in the removal of significant percentage of SO_4 ions and their replacement with OH ions. As a result of this exchange, the pH of the water changes from pH 2.85 to approximately pH 5 to 5.5. Additionally, this SO_4/OH ion replacement results in the formation of metal hydroxides of Fe, Cu, Al, and Zn, which are insoluble in water at the neutral pH and which will form a precipitate.

As a result of Stage 1 precipitation, the removal of >99% of Al, Fe, Cu, Zn, and Se is achieved.

Coprecipitation of approximately 25 to 30% of Mg and 30 to 50% of Cd also take place at stage 1. Additionally, a very small adsorption of Na and Ca take place as a result of the precipitation processes taking place at Stage 1.

C.4 Metal Hydroxide Separation

Insoluble metal hydroxides and the depleted anion-exchange resin (now in the RSO_4 form) are transported to Apparatus 2 and 7. The precipitate and depleted ion-exchange resin will be filtered from the ongoing process stream through the use of drum/vacuum extraction, conventional filtering, and/or settling techniques as a practical method of satisfying throughput requirements. Because they are soluble at pH 5 to 5.5, sulfates of Mn, Mg, Ca, and Na will not precipitate in Stage 1 but will be directed to Stage 2 where these elements will be later extracted.

The sludge containing metal hydroxides of Fe, Cu, Al, and Zn and depleted ionite are treated with sulfuric acid at Apparatus 7, resulting in conversion of the metal hydroxides into metal

Figure C1. Process flow diagram.

Table C-1. Target ionic components

Element	On RRP List	In Pit mg/L	Statute Max. mg/L	Actual >Statute = Removal	Butte Demo
Al	XX	260	2	Must	Separation
As	XX	0.8	0.36	Must	Removal
Ca		456		\$Value?	Separation
Cd	XX	2.14	0.01	Must	Removal
Cu	XX	172	1.3	Must	Separation
Fe	XX	1,068	1	Must	Separation
Mg		409		\$Value?	Separation
Mn	XX	185	0.05	Must	Separation
Na		76.5		\$Value?	Removal

Se	XX	0.4	0.26	Must	Removal
SO ₄	XX	7,600	500	Must	Removal
Zn	XX	550	5	Must	Separation
*RRP=Resource Recovery Project					

sulfates in concentrated solution. The resin component of the input sludge is thus separated from its commingled precipitate with these liberated resins being sent to Apparatus 4 for a proprietary regeneration process resulting in ROH form resin with special chemical properties. Regenerated resins are returned to Apparatus 1 where they are used again as the primary agent causing pH change and precipitation of input Berkeley Pit AMD.

From the solution of mixed sulfates of Fe, Al, Zn, and Cu produced at Apparatus 7 after dissolution of the precipitate of their hydroxides (see paragraph 2.2.2 of the Final Report), high purity (99.7%) Cu is obtained by the adding Fe scrap and known processes of cementation. Solid Cu thus produced is filtered from the remaining solution of Al, Zn, and Fe sulfates.

This combined sulfate solution stream, less Cu, is directed to Stage 7 of the process for the separation of its remaining constituent compounds. Separation of these sulfate compounds is effected with the use of proprietary techniques based on differences in molecular sorption of sulfates of metals by an ion exchanger. One of the features of this proprietary process is the fact that its efficiency increases as the concentration of the solution increases; therefore the solution is recycled internally until the desired degree of purity and concentration is achieved.

The separation process performed in Apparatus 7 results in pure concentrations of Fe^{3+} , Al^{3+} , and Zn^{2+} in sulfate form.

C.5 Processing of Solution Containing Compounds of Mn, Mg, Ca, and Na.

The pH 5 to 5.5 solution containing sulfates of Mn, Mg, Ca, and Na that remains after the precipitation processes in Stages 1 and 2 is processed in the final section of Stage 2. Processing herein is designed to remove all Mn

and Mg present in the process stream. The technique of processing is selective precipitation in either a batch or continuous mode of operation. Centrifugal or settling and/or filtration techniques will be used to extract the precipitates at the appropriate points of the process.

Manganese in its hydroxide form is extracted to below detectable levels as the first step in Stage 2. Cd not extracted at Stage 1 with Al, Fe, Cu, and Zn is coprecipitated then in Stage 2 with the Mn. Also, insignificant amounts of Mg, Ca, and Na are also coprecipitated during Stage 2 of the process.

The process solution, less Mn, is directed to the second step of Stage 2, where Mg in its hydroxide form is extracted to below detectable levels. Insignificant amounts of Na and Ca are also coprecipitated in this second step of Stage 2.

The solution after recovery of Mg is treated in an ion-exchange column where sulfates of Ca and Na are converted to Ca and Na hydroxides and the resultant process stream is directed to Stage 3.

C.6 Processing of Solution Containing Compounds of Ca and Na.

The first operation in Stage 3 results in the extraction of Ca in a column with cation-exchange resin in the Na form an Na form of cation exchanger (See section 2.2.4 of the Final Report) that is obtained from the successive operation in Stage 3. The Ca is then isolated as precipitate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum) at the regeneration of the cation exchanger with H_2SO_4 in a proprietary apparatus. The output solution from this first operation contains primarily sodium hydroxide, and this solution is passed to the second part of Stage 3 where NaOH is removed using a traditional ion-

exchange column on cation-exchange resins of the H^+ form.

Calcium and Na are removed from the process stream in sequential fashion with Ca being removed first. There is no statutory reason for the removal of Ca and Na ions from the output waterstream as no standards have been established for these two elements. However, to ensure “low” levels of these ions and the removal of any remaining micro-amounts of heavy metals in hydroxide form, two final “polishing” operations are employed. Both these operations are contained in Stage 3 of the PIT process.

The ion-exchange reaction in Apparatus 3 results in the production of de-mineralized, de-ionized water for either industrial, agricultural, or human utilization. At this point water leaving this cation-exchange process will be compliant with applicable Federal, State, and local standards for waters to be discharged into the aquifer.

C.7 Regeneration of Ion-Exchange Resins

Depleted ion-exchange resins from Apparatus 1 and 3 are passed to proprietary counter-current resin regeneration processes in Apparatus 4 and 5. The anion-exchange resin is treated with sodium hydroxide solution in Apparatus 4, and the cation-exchange resin is treated with sulfuric acid in apparatus 5 in proprietary processes developed by the project team. Additional proprietary operations related to flushing, rinsing, and elution are performed on these resins during the regeneration processes, resulting in ionites of the properties required by Stages 1 and 3.

The regeneration of anion-exchange resins is accomplished with NaOH from the electrolyzer and results in production of Na_2SO_4 , which is directed to the electrolyzer where it is converted into NaOH and H_2SO_4 . It is anticipated that some micro-amounts of metals will be eluted in the regeneration of cation-exchange resins and passed to the electrolyzer.

Regeneration of the cation exchanger is accomplished with H_2SO_4 from the electrolyzer and results in production of a gypsum precipitate ($CaSO_4 \cdot 2H_2O$) and a solution of sodium sulfate (Na_2SO_4). The solution of $NaSO_4$ is directed to the electrolyzer.

Regeneration of the ion-exchange resins in counter-current columns results in a reduced amount of ion-exchange resin being used in the process and further decreases the equipment volumes.

C.8 Material Balance

A summary diagram of the demonstrated process with calculated estimations of input and output material balances is presented below.

Figure C-2 is a summary diagram of demonstrated technological process (with accurate estimations of material balances).

Figure C-2. Summary diagram of demonstrated technological processes.